UNIVERSITÉ DU QUÉBEC À MONTRÉAL

AUGMENTATION RÉCENTE DE LA PRODUCTIVITÉ PRIMAIRE ET DES FLUX DE CARBONE DANS L'ESTUAIRE MARITIME DU SAINT-LAURENT : ÉVIDENCES MICROPALEONTOLOGIQUES ET GÉOCHIMIQUES

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RECENT EUTROPHICATION AND CONSEQUENT HYPOXIA IN THE BOTTOM WATERS OF THE LOWER ST. LAWRENCE ESTUARY: MICROPALEONTOLOGICAL AND GEOCHEMICAL EVIDENCE

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AVANT-PROPOS

Ce mémoire de maîtrise a été rédigé sous forme d'article scientifique qui a été accepté sous condition par la revue *Marine Geology*. La langue anglaise a donc été utilisée et la mise en forme respecte les exigences de *Marine Geology*. Les figures citées dans l'article ont été placées à la suite des références. Deux autres auteurs ont participé à la rédaction de cet article, Anne de Vernal et Alfonso Mucci, respectivement professeur au département des Sciences de la Terre et de l'atmosphère de l'UQAM et au Earth and Planetary Sciences département de l'Université McGill.

Vu l'imposante banque de donnée recueillie et compilée durant ce travail les tableaux de comptages et autres données sont disponible électroniquement sur un disque compact joint ou à thibodeau.benoit@courrier.uqam.ca.

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LISTE DES ABRÉVIATIONS

AR :	Accumulation rate
BSPP :	Brigantedinium spp
CT :	Calcareous tests
EMSL :	Estuaire maritime du Saint-Laurent
LSLE :	Lower St. Lawrence estuary
IMIC :	Islandinium? cezare
IMIN :	Islandinium minutum
MAR :	Mass accumulation rate
NLAB :	Nematosphaeropsis labyryrinthus
OC :	Organic carbon
OCEN:	Operculiodinium centrocarpum
OL :	Organic linings
PDAL:	Pentapharsodinium dalei
PERI:	Protoperidiniales
SELO:	Spiniferites elongatus
SQUA:	Selenophemphix quanta
SRAM:	Spiniferites ramosus
TC :	Total carbon
TN :	Total nitrogen

RÉSUMÉ

De récentes études ont démontré que plus de 1300 km^2 du fond du chenal laurentien sont baignés par des eaux dont les concentrations d'oxygène dissous sont en deçà de 62.5 µM ou 2 mg/l, correspondant au seuil qui définit l'hypoxie. Une des causes possibles du développement de l'hypoxie serait l'eutrophisation des eaux de surface liée à l'augmentation de l'activité agricole et industrielle dans les Basses-Terres du Saint-Laurent. Les apports accrus en nitrates rendraient compte d'une productivité primaire et d'un flux de carbone organique croissant. La dégradation de cette matière organique exportée dans les eaux profondes pourrait contribuer à l'appauvrissement progressif de celles-ci en O_2 dissous.

Dans ce contexte, nous avons analysé les sédiments de deux carottes récoltées le long du chenal laurentien entre Tadoussac et Les Méchins afin de retracer les variations de productivité depuis le dernier siècle et ainsi, de vérifier si ceux-ci révèlent des indices d'une eutrophisation.

Les résultats obtenus (carotte boîte AH00-2220; 48°38,33'N, 68°37,82'W; 324m et CR02-23; 48°42.008'N/68°38.894'W; 345m) révèlent une augmentation récente (après 1960 AD) du δ^{13}Corg que nous interprétons comme une augmentation des apports de matière organique marine. De la même façon et sur le même intervalle de temps, la concentration des kystes de dinoflagellés augmente, tout comme leurs flux, ce qui pourrait refléter un accroissement de la productivité primaire. Nous notons aussi une tendance semblable dans la concentration et du flux de réseaux organiques de foraminifères qui reflète probablement un accroissement de la productivité benthique liée à l'augmentation du flux de matière organique aux sédiments. Les concentrations et les flux de tests de foraminifères benthiques sont caractérisés par la même tendance d'augmentation récente. Nous notons aussi l'apparition et l'augmentation progressive de la présence des taxons Brizalina subaneriensis et Bulimina exilis entre les années 1960 et 1970. Ces taxons se singularisent par leur forte tolérance aux faibles concentrations d'oxygène et aux flux de carbone élevés.

Les résultats obtenus dans cette étude appuient l'hypothèse d'une augmentation des flux sédimentaires de matière organique marine associés à une augmentation de la productivité primaire dans cette partie de l'estuaire du St-Laurent. Cette augmentation de productivité pourrait bien être un facteur important dans la diminution récente des teneurs en oxygène dissous, il est donc important d'explorer plus en détail cette hypothèse afin de mieux connaître les mécanismes en cours dans l'estuaire du St-Laurent et leur relation avec l'hypoxie récente des eaux de fond.

Mots clés : Hypoxie, eutrophication, foraminifères, géochimie, Saint-Laurent

ABSTRACT

Recent measurements of dissolved oxygen (DO) concentrations in the bottom waters of the Lower St. Lawrence Estuary (LSLE) show that about 1300 km2 of the Laurentian Channel (LC) is now bathed by hypoxic waters (i.e., waters containing less than 62.5 μM or 2 mg/l of dissolved oxygen). A compilation of historical DO measurements of waters taken between 300 and 355 m depth in the Lower St. Lawrence Estuary reveals that DO concentrations have decreased by nearly 50% over the last 70 years. The deep waters of the LC are isolated from the atmosphere by a sharp, permanent pycnocline that begins around 100 - 150 m depth. At depths greater than 150 m the oxygen lost cannot even be replenished by winter convection but only by weak diffusion from the overlying water or by tidal mixing at the head of the LC. For this reason, the oxygen balance is precarious: increased organic carbon fluxes and respiration and/or decreased deep estuarine landward flow will lead to lower oxygen concentrations. Eutrophication is one of the possible causes of hypoxia. An increased flux of nutrients from the watershed would lead to an increase surface productivity and organic carbon flux to the bottom waters. The microbially-mediated remineralization of this organic carbon could contribute to the progressive depletion of dissolved oxygen in the bottom waters. Micropaleontological and geochemical analyses were carried out on two sediment box cores (AH00-2220 and CR02-23) recovered in the Lower St. Lawrence Estuary (LSLE) in order to document recent temporal variations of primary productivity and carbon fluxes to the bottom waters. These reveal a ten-fold increase in the accumulation rate of dinoflagellate cysts and benthic foraminifera in the sediment over the last four decades which can be interpreted as a recent increase in pelagic and benthic production. Furthermore, the appearance of the benthic foraminiferal species *Brizalina subaenariensis* and *Bulimina exilis*, which are tolerant of low oxygen concentrations and high organic fluxes, in the upper 20 cm of the cores, may reflect significant changes in bottom water conditions over the last 40 years. Variations in the microfossil abundances in core AH00-2220 are strongly correlated with an increase in organic carbon (OC) content (from 1.1 to 1.6%) and to a shift in the isotopic signature of the latter ($\delta^{13}C_{ORG}$ from -24.8 to -24.0‰). Similarly, a concomitant decrease in the C_{ORG}:N ratio (from 15 to 12), an increase in organic carbon content (from 1.3 to 1.9%) and an increase in $\delta^{13}C_{ORG}$ (from -24.5 to -23.5‰) were observed in core CR02-23, all of which suggest an enhanced accumulation of marine over terrestrial OC in the LSLE. Our results imply that a significant increase in marine productivity in the LSLE occurred since the 1960's.

Keywords: Lower St. Lawrence Estuary, eutrophication, hypoxia, dinoflagellate cysts, benthic foraminifera, geochemistry.

INTRODUCTION

L'hypoxie naturelle est un phénomène assez courant dans plusieurs environnements côtiers caractérisés par une circulation profonde restreinte comme les fjords. Par contre, on note de plus en plus l'apparition de zones hypoxiques dans les environnements côtiers et estuariens. L'apparition de ces zones est souvent associée à l'apport anthropogénique de nutriments et l'eutrophisation côtière (Cloern, 2001; Diaz 1995; Gray, 2002).

Des mesures récentes de teneur en oxygène dissous dans les eaux de fond de l'estuaire maritime du St-Laurent (EMSL) montrent qu'une superficie d'environ 1300 km^2 du chenal laurentien est maintenant baignées par des eaux hypoxiques (contenant moins de 62.5 µM/l ou 2mg/l d'oxygène dissous (Diaz et Rosenberg, 1995). Une compilation des données historiques des mesures d'oxygène dissous prises entre 300 et 355 mètres dans l'EMSL révèle que les concentrations d'oxygène dissous ont diminué de près de 50% au cours des derniers 70 ans (Gilbert et al., 2005).

L'eutrophisation consiste en une augmentation du flux de nutriments lessivés du bassin versant vers l'estuaire, ce qui permet une plus forte prolifération du phytoplancton et conséquemment une plus forte exportation de carbone organique vers les eaux de fond. La dégradation de ce carbone organique par la réaction de respiration peut contribuer à la diminution progressive de la concentration en oxygène dissous dans les eaux de fond. Dans la présente étude nous avons analysé des carottes de sédiment prises dans l'EMSL afin de reconstruire l'historique de la productivité de surface depuis le dernier siècle et identifié les signes d'eutrophisation récente.

Il existe plusieurs indicateurs d'eutrophisation : la pénétration de la lumière, la concentration de chlorophylle a, le taux de croissance des épiphytes versus celui des macrophytes, les changements dans la population de protistes alguaires (des diatomées aux dinoflagellés, des benthiques aux pélagiques) et l'augmentation de la décomposition de la matière organique (Livingston, 2000). Par contre les séries de

données instrumentales de ces paramètres sont limitées à quelques années voir quelques dizaines d'années. Il est donc important de développer des indicateurs d'eutrophisation à partir de l'étude du sédiment pour obtenir des séries temporelles qui permettent de cerner l'évolution du milieu et en dégager les tendances à long terme afin de déterminer si l'hypoxie récente de l'EMSL est due à des variations naturelles ou aux activités humaines.

La distribution de l'oxygène dissous dans les différentes masses d'eaux de l'EMSL (deux en hiver et trois le reste de l'année) est dépendante de la structure thermohaline de celles-ci. La circulation des masses d'eaux est de type estuarienne, c'est-à-dire des eaux douces de surface qui se déversent vers l'océan et des eaux de fond froides venant de l'Atlantique. La couche de surface est bien oxygénée puisqu'elle est en contact avec l'atmosphère, la couche intermédiaire froide se développe par convection au printemps et se mélange aux eaux de surface durant l'hiver. Les eaux de fond proviennent d'un mélange des eaux du Courant du Labrador et des eaux de l'Atlantique Nord Central et sont isolées de l'atmosphère par une pycnocline permanente. Étant isolée de l'atmosphère, les eaux de fond s'appauvrissent graduellement en oxygène dissous de par la respiration et la reminéralisation de la matière organique provenant des eaux de surfaces, c'est pourquoi la concentration d'oxygène dans ces eaux est précaire et que toute augmentation des flux de carbone organique ou du taux de respiration peut entraîner une diminution critique de la teneur en oxygène dissous.

Nous avons étudié les variations passées de la productivité de l'EMSL en utilisant plusieurs indicateurs micropaléontologiques et géochimiques du sédiment. Parmis eux les kystes de dinoflagellé qui ont déjà été utiliser comme indicateur de la productivité primaire et de la disponibilité des nutriments dans des assemblages modernes (Devillers et de Vernal, 2000; Radi et de Vernal, 2004) et appliqué à des séquence sédimentaire holocènes des fjords scandinaves (Dale, 1994; Thorsen etDale, 1997; Dale, 2001), de la mer Adriatique (Sangiorgi and Donders, 2004) et des côtes nord-est des Etats-Unis (Pospelova et al., 2002; Verardo, 1999). L'abondance et la

taxonomie des foraminifères benthiques ont été utilisées pour estimer qualitativement la productivité benthiques et les conditions d'oxygénation (Loubere, 1991; Mackensen et al., 1993; Sen Gupta, 1996; Bernhard, 1997; Karlsen et al., 2000; Osterman, 2003; Platon et al., 2005). Ces données ont été couplées avec des mesures géochimiques, incluant la teneur en carbone organique du sédiment, la signature isotopique du carbone organique ($\delta^{13}C$) et le rapport carbone sur azote (C:N) qui nous renseignent sur la provenance de la matière organique (Meyers, 1994; Struck et al., 2000; Voss et al, 2000; Zimmerman and Canuel, 2000; Bratton et al., 2003; McKay et al., 2004).

CHAPITRE I

RECENT EUTROPHICATION AND CONSEQUENT HYPOXIA IN THE BOTTOM WATERS OF THE LOWER ST-LAWRENCE ESTUARY : MICROPALEONTOLOGICAL AND GEOCHEMICAL EVIDENCE

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Abstract

Micropaleontological and geochemical analyses were carried out on two sediment box cores (AH00-2220 and CR02-23) recovered in the Lower St. Lawrence Estuary (LSLE) in order to document recent temporal variations of primary productivity and carbon fluxes to the bottom waters. These reveal a ten-fold increase in the accumulation rate of dinoflagellate cysts and benthic foraminifera in the sediment over the last four decades which can be interpreted as a recent increase in pelagic and benthic production. Furthermore, the appearance of the benthic foraminiferal species *Brizalina subaenariensis* and *Bulimina exilis*, which are tolerant of low oxygen concentrations and high organic fluxes, in the upper 20 cm of the cores, may reflect significant changes in bottom water conditions over the last 40 years. Variations in the microfossil abundances in core AH00-2220 are strongly correlated with an increase in organic carbon (OC) content (from 1.1 to 1.6%) and to a shift in the isotopic signature of the latter ($\delta^{13}C_{ORG}$ from -24.8 to -24.0‰). Similarly, a concomitant decrease in the C_{ORG}:N ratio (from 15 to 12), an increase in organic carbon content (from 1.3 to 1.9%) and an increase in $\delta^{13}C_{ORG}$ (from -24.5 to -23.5‰) were observed in core CR02-23, all of which suggest an enhanced accumulation of marine over terrestrial OC in the LSLE. Our results imply that a significant increase in marine productivity in the LSLE occurred since the 1960's.

Keywords: Lower St. Lawrence Estuary, eutrophication, hypoxia, dinoflagellate cysts, benthic foraminifera, geochemistry.

1. Introduction

Hypoxia occurs naturally in many coastal environments with restricted circulation, such as fjords and inland seas, but the recent proliferation of hypoxic zones along inhabited coastlines and estuaries appears to be linked to anthropogenic nutrient

loading and coastal eutrophication (Cloern, 2001; Colman and Bratton, 2003, Diaz and Rosenberg, 1995; Gray et al., 2002, Turner and Rabalais, 1994). Severe hypoxia is defined as the threshold below which significant impacts on the biota can be observed and corresponds to dissolved oxygen concentrations below 62.5 μM or 2 mg/L (Diaz and Rosenberg, 1995; Rabalais et al., 2001). In most cases, increased discharge of nutrients (especially nitrate) in coastal and estuarine environments enhances primary productivity which, in turn, increases the flux of organic carbon (OC) to the bottom waters and the mass accumulation rate (MAR) of OC in sediments. The microbially-mediated remineralization of this organic carbon can contribute to the progressive depletion of dissolved oxygen in the bottom waters in a stratified body of water.

A number of indicators of present day eutrophication have been identified: light penetration depth, chlorophyll *a* concentration, epiphytic *versus* macroalgal growth rates, changes in algal community composition (diatoms to dinoflagellates, benthic to pelagic) and the increased remineralization rate of organic matter (Livingston, 2000). Unfortunately, time series longer than 30 years are not available for these parameters in most coastal environments. It is, therefore, critical to develop and apply proxies of eutrophication in order to reconstruct historical variations of primary productivity and determine if recent hypoxia results from natural variations or anthropogenic activities that foster the export of limiting nutrients.

Recent measurements of dissolved oxygen (DO) concentrations in the bottom waters of the LSLE show that about 1300 km^2 of the Laurentian Channel (LC) are now permanently bathed by hypoxic waters (Gilbert et al., 2005). A compilation of historical DO measurements of waters taken between 300 and 355 m depth in the LSLE reveals that DO concentrations have decreased by nearly 50% over the last 70 years, from 125 μM in the 1930s to an average value of 65 μM for the 1984-2003 period (Gilbert et al., 2005). Preliminary results on the distribution of redox-sensitive elements (e.g., U, Mo, Re) in a long core (i.e., MD99-2220) recovered in the LSLE

show no evidence of pre-anthropogenic anoxia in this area over the Holocene (G. Chaillou, pers. comm.).

In this paper, we use micropaleontological and geochemical proxies recorded in the sediments to reconstruct past variations in productivity in the LSLE. Among these, the abundance and assemblages of dinoflagellate cysts serve as proxies of primary production and nutrient availability as documented from the modern assemblage (c.f. Devillers and de Vernal, 2000; Radi and de Vernal, 2004) and applied to the late Holocene sedimentary sequences of the Scandinavian fjords (Dale, 1994; Thorsen and Dale, 1997; Dale, 2001), the north-western Adriatic Sea (Sangiorgi and Donders, 2004), and along the NE US coast (Pospelova et al., 2002; Verardo, 1999). The abundance and taxonomy of benthic foraminifera are also used to qualitatively assess the benthic oxygen demand since they are sensitive to the OC flux and bottom water oxygenation (Loubere, 1991; Mackensen et al., 1993; Sen Gupta, 1996; Bernhard, 1997; Karlsen et al., 2000; Osterman, 2003; Platon et al., 2005). These data are coupled to geochemical measurements, including the organic carbon content, its isotopic signature ($\delta^{13}C_{ORG}$) and the C_{ORG}:N ratio to identify the origin and nature of the organic matter preserved in the sediment (Meyers, 1994; Struck et al., 2000; Voss et al, 2000; Zimmerman and Canuel, 2000; Bratton et al., 2003; McKay et al., 2004). The objective is to qualitatively reconstruct temporal variations of primary productivity and to link these to the dissolved oxygen record.

2. Study area

2.1 Water masses

The St. Lawrence Estuary and Gulf of St. Lawrence form part of the second largest freshwater system in the world (freshwater discharge of 10 900m^3 s^{-1}) (Bourgault and Koutitonsky, 1999). The dominant topographic feature of this maritime system is the

Laurentian Channel (LC), a submarine valley, 250-500 m deep, that extends over 1240 km landward from the continental shelf edge of the eastern Canadian coast to Tadoussac (Figure 1). The circulation is estuarine and is characterized by three water layers: 1) a thin surface layer (down to 50 m) of low salinity water (~25) that flows seaward and originates from mixing of seawater with freshwater runoff from the Great Lakes, St. Lawrence and Northern Quebec river drainage system, 2) a seasonal intermediate, cold and saline (32-34) layer that is present between 50 and 150 m, and 3) a warmer and saltier (>34) deep layer that flows landward and is a mixture of the Labrador Current and North Central Atlantic waters (Dickie and Trites, 1983).

2.2 The oxygen balance

The deep waters of the LC are isolated from the atmosphere by a permanent pycnocline situated between 100 - 150 m depth. Under these conditions, the bottom waters gradually lose oxygen through respiration and remineralization of organic matter that settles through the water column as they flow landward from the mouth of the LC to its head near Tadoussac. The estimated time it takes for a parcel of water entering the mouth of the LC at 250 m depth to reach its head is 3-4 years (Gilbert et al., 2005). At depths greater than 150 m, the oxygen consumed through respiration cannot even be replenished by winter convection (Petrie, 1996). For this reason, the oxygen balance is precarious: increased organic carbon fluxes and respiration and/or decreased landward flow (or increased residence time) will lead to lower oxygen concentrations.

Based on a detailed analysis of archival data, Gilbert et al. (2005) proposed that between one half and two-thirds of the 60 μM decline in dissolved oxygen concentration and a concurrent 1.65°C warming of the bottom waters of the LSLE in the last seven decades are attributable to a decreasing proportion of oxygen-rich Labrador Current Water in the water mass entering the Gulf of St. Lawrence from the northwest Atlantic Ocean. A discussion of the changes of the circulation pattern in

the Northwestern Atlantic that impinge on the deep estuary ventilation can be found in Gilbert et al. (2005). Because of the precarious oxygen balance in the LSLE, increased primary productivity and organic carbon fluxes to the bottom waters could account for the remainder of the dissolved oxygen decline due to increased oxygen consumption. Benoit et al. (2006) developed a 2-D coupled advection-diffusion-diagenetic model that emphasizes the role of organic carbon oxic mineralization in generating hypoxic bottom waters in the LSLE.

2.3 Land use history

Since the European settlement in the 17th century, the rate of agricultural growth and land clearing increased and reached a maximum in the second half of the 20th century concomitantly with industrial development in Eastern Canada, notably the paper mill industry. These activities resulted in increased discharge of both nutrients (by soil erosion) and terrigenous organic carbon (by paper mills waste) to the LSLE. A historical record of the amount of fertilizers sold (and used) locally reveals a 70% increase between 1970 and 1988 followed by a modest decrease. Figure 2 shows how well the two variables are correlated with the DO content of the LSLE bottom waters.

3. Material and methods

3.1 Coring sites and on-board sampling

Sediment samples were collected in August 2000 (AH00-2220, 48°38.33N/68°37.82W; 324m) and September 2002 (CR02-23, 48°42.008'N/68°38.894'W; 345m) on the R/V Alcide C. Horth in the LSLE (Figure 1). Undisturbed sediments were recovered with an Ocean Instrument Mark II box corer. The core (0.12 m^2 x 0.5 m long) was immediately transferred to a custom holding table (Edenborn et al., 1986) and sampled at one centimeter intervals as the sediment was sequentially exposed by step-wise lowering of the front plate. Core AH00-2220 was recovered from the southern margin of the LC whereas CR02-23

was taken on the northern margin. Despite the short distance (i.e., 9 km) separating the two sites, significant differences in the surface water properties and circulation patterns (El-Sabh and Silverberg, 1990) may influence the flux and nature of the organic matter settling from the surface and, thus, the sedimentary record.

3.2 Chronology and accumulation rates

Lead-210 activities of dried and crushed samples were obtained indirectly by measuring the decay rate of its daughter isotope ^{210}Po ($t_{1/2}$ = 138.4 days; α = 5.30 MeV) by alpha spectrometry. The measurements were carried out more than 6 months after sampling to ensure that secular equilibrium had been reached. A ^{209}Po spike was added to the samples to determine the extraction and counting efficiencies. Polonium was extracted from the sediment and purified by chemical treatments (reacted sequentially with HCl, HNO_3, HF and H_2O_2) and deposited on a silver disk (Flynn, 1968). The $^{209\text{-}210}Po$ activities were measured in a silicon surface-barrier α-spectrometer (EGG&ORTEC type 576A). The excess ^{210}Pb activity was obtained by subtracting the supported regional (i.e., LSLE) activity value of 1.00 ± 0.08 dpm/g (Zhang, 2000). Sedimentation rates (constant rate supply model) were calculated using the radioactive decay constant (λ) of ^{210}Pb and the linear regression slope of the logarithmic function of excess ^{210}Pb.

Cesium-137 was measured by γ-ray spectrometry at 661.6 keV, using a low-background high purity Ge well-detector (Canberra). Replicate analyses (n=6) of the standard reference material IAEA-300 (Baltic Sea sediment) confirmed the reproducibility (~±1%) of the measured ^{137}Cs activities.

3.3 Micropaleontological analyses

3.3.1 Palynomorphs

Sediment samples were treated according to the method described by de Vernal et al. (1999). Briefly, the sediment was washed through 106 and 10 μm sieves to eliminate clay-sized and coarse grained particles. The 10-106 μm size fraction was reacted sequentially with warm hydrochloric acid (HCl 10%) and warm hydrofluoric acid (HF 49%) to dissolve, respectively, carbonate and silicate phases. The residual solids were mounted between slides and cover-plates for optical microscopic analyses at 400x to 1000x magnification.

The concentration of palynomorphs was estimated based on the marker grain method (Matthews, 1969). The addition of a known number of exotic grains (*Lycopodium* spores) to each sample permits the evaluation of absolute concentrations from the relative counts of the marker grains and palynomorphs. The reproducibility of the counts was estimated at ±10% at the 95% confidence interval (de Vernal et al., 1987). All palynomorphs (i.e., dinocysts, organic linings of benthic foraminifera, pollen grains and spores) were counted in samples from core AH00-2200. Only dinocysts and organic linings of benthic foraminifera were counted in core CR02-23. The dinocyst nomenclature conforms to that reported in Rochon et al. (1999).

In this paper, we report concentrations and accumulation rates of dinocysts and organic linings of benthic foraminifera as well as the relative abundances of the main dinocyst taxa. Detailed palynological data can be found in Thibodeau (2005). Taxonomic affinities between the organic linings (OL) and the calcareous tests (CT) of benthic foraminifera were demonstrated from laboratory experiments (de Vernal et al., 1992; Leduc et al., 2002).

3.3.2 Benthic foraminiferal tests

For each subsample, five cm^3 of sediment were dried at room temperature, weighed, and washed through a 106 μm screen. The residual fraction was examined under a binocular microscope (20x). The <106 μm fraction was not examined to avoid small size tests and juvenile forms that are often difficult to identify. All foraminiferal tests, including calcareous and agglutinated forms, were hand-picked, identified and counted. The nomenclature of Rodrigues (1980) was adopted.

The concentration, accumulation rates and relative abundances of the most abundant taxa (*Brizalina subaenariensis*, *Globobulimina auriculata, Bulimina marginata* and *Bulimina exilis*) are reported here whereas data for other taxa can be found in Thibodeau (2005).

3.4 Carbon analyses (TOC/TIC, $\delta^{13}C$, C:N)

The total carbon (TC) and total nitrogen (TN) contents of an aliquot (5 to 10mg) of the dried, crushed and homogenized sediment samples were determined with a Carlo Erba™ NC 2500 elemental analyzer. Total inorganic carbon (TIC) was analyzed independently using a UIC Coulometrics coulometer following acidification of the samples and CO_2 extraction. Total organic carbon (TOC) was obtained by difference (i.e., TC minus TIC). Precision, as determined from replicate measurements of Organic Analytical Standard substances (Acetanilide, Atropine, Cyclohexanone-2,4-Dinitrophenyl-Hydrazone and Urea), are estimated at ± 0.1% for OC and ± 0.3% for N contents. The analytical reproducibility is 5%.

Sediment samples were acidified with 1N HCl, dried, crushed, and homogenized before isotopic analysis of the organic carbon (OC). The isotopic composition of the OC was measured with a Carlo Erba™ elemental analyzer inline with a GV Instruments IsoPrime™ mass spectrometer. Data are reported in the δ notation in ‰ with reference to V-PDB (Coplen, 1995) and the analytical uncertainty is ± 0.1 ‰. The international standard IAEA-C6 sucrose was measured several times during the

isotopic analyses and yielded an average value of -10.8 ± 0.1 ‰ (n=8) whereas the reported value is -10.8 ‰. The isotopic composition of nitrogen ($\delta^{15}N$) was not measured due to the very low (~0.14 % W/W) nitrogen content of the sediments.

3.6 Microfossil accumulation rate estimates

The accumulation rate (AR) is reported as the number of microfossils per square centimetre per year. It was calculated using the sedimentation rate (cm/yr) and the concentrations of cysts per cm^3 of wet sediment in core AH00-2220. Given the ambiguity of the sedimentation rate below 12 cm in core CR02-23, we did not attempt to calculate AR.

4. Results

4.1 Core AH00-2220

4.1.1. Excess ^{210}Pb, ^{137}Cs activity and sedimentation rates

The excess ^{210}Pb activity ($^{210}Pb_{ex}$) of the sediments, expressed on a logarithmic scale, shows uniform values in the upper 5 cm of the core (Figure 3). This interval corresponds to the zone of active bioturbation. The $\ln(^{210}Pb_{ex})$ data in the 5 to 30 cm interval can be fit reasonably well to a simple linear equation with a slope of -0.062 (r^2 = 0.91), corresponding to a sedimentation rate of about 0.50 (± 0.01) cm/yr. Artificial radionuclides such as ^{137}Cs originated from atmospheric nuclear tests carried out during the 1952-1972 period with maximum activities corresponding to the year 1963 (Jouanneau et al., 1999). Measurements of ^{137}Cs activity and the peak at ~18 cm (Figure 3) are consistent with the sedimentation rate estimated from the $^{210}Pb_{ex}$ activities.

According to our age model (Figure 3), the upper 30 cm would represent approximately 60 years of sedimentation (i.e., 1940-2000 AD). Below 30 cm, the sedimentation rate could be assumed to be identical to the one derived from the 5 to 30 cm interval or estimated from the age model established on the basis of ^{14}C measurements (n=9) by St-Onge et al. (2003) in a long piston core (i.e., MD99-2220) recovered in 1999 at the box core site. In the latter age model, sedimentation rates are nearly invariant at 0.15 cm/year for the last 8000 years. Thus, below 30 cm, the sedimentation rates might possibly range between 0.15 and 0.50 cm/yr. Because of poor chronological control, we did not attempt to evaluate AR for the lower section of core AH00-2220.

4.1.2. Dinocyst assemblages

Dinocyst concentrations vary from 2000 to 5000 cysts/g (Figure 4). The data reveal a very significant upward increase of the dinocyst accumulation rate (AR) over the 0-20 cm interval, from approximately 500 to 1500 cysts*cm^{-2}*yr^{-1}. These results may be interpreted as a significant increase in planktonic productivity over the last decades. Preliminary results of biogenic silica extractions (A. Mucci, pers. comm) on a core taken close (48°42.11'N/68°38.94'W; 350m) to AH00-2220 show no systematic trends or variations in concentrations (0.17-0.37% W/W) over the 3 to 40 cm depth interval and a sharp increase in the top 2 cm (0.87%). On the other hand, a historical compilation of dissolved silica concentrations in the bottom waters (i.e., > 300 m) of the LSLE reveals a significant increase since 1960 (from 18 to 55 μM; D. Gilbert, pers. comm). These data are not consistent with a recent change in ecology (nitrate vs silicate depleted) or the type of planktonic productivity (dinoflagellate vs diatoms) in surface waters but possibly point to an overall increase in pelagic productivity over past four decades.

The dinocysts assemblages are dominated throughout the core by heterotrophic taxa belonging to the genus *Brigantedinium* (25 to 45%) and by the autotrophic taxon

Pentapharsodinium dalei (25 to 55%). In addition to *Brigantedinium* spp., many other heterotrophic taxa are present. They include *Selenophemphix quanta*, *Islandinium minutum, Islandinium? cezare*, and unidentified *Protoperidinium*-type dark brown cysts which were grouped as "undifferentiated Protoperidinioids". The autotrophic assemblages include *Nematosphaeropsis labyrinthus, Operculodinium centrocarpum* and a few specimens of *Spiniferites elongatus.* No major change could be resolved in the composition of the assemblages, except a decrease of *Pentapharsodinium dalei* (40 to 20%) and a concomitant increase of *Operculodinium centrocarpum* (2 to 10%) in the top 15 cm of the core. All others species show high frequency oscillations, but no clear trend. The ratio of dinocysts to pollen grain shows the same trend as the concentration and AR of dinocysts and, thus, confirm that the observed trend does not result from differential dilution by other sediment components.

4.1.3. Benthic foraminiferal assemblages

The concentration and AR of benthic foraminifera also increase towards the sediment-water interface in core AH00-2220 (Figure 5). Concentrations are fairly constant (~3 to 7 tests/g) in the lower part of the core (i.e., below 30 cm) and increase up to 40 tests/g in the upper part of the core. The AR displays a similar trend, with uniform values ranging between 1 and 5 tests*cm^{-2}*yr^{-1} in the 10-30 cm interval and a significant increase up to 10 to 15 tests*cm^{-2}*yr^{-1} in the upper part of the core. The AR of foraminifera organic linings recovered from palynological preparations also displays a significant increase in the upper part of the core. In contrast to the uncertainties related to the preservation of foraminifera shells (i.e., dissolution during oxic diagenesis), variations in the abundance of organic linings can be clearly interpreted as a recent increase in benthic foraminifera production.

The foraminifera tests assemblages are characterized by low species diversity, with only 4 species accounting for more than 95% of the total abundance. The dominant

species in the 20-50 cm interval is *Globobulimina auriculata* (30-100%). *Bulimina marginata* is present throughout the core but shows large relative abundance variations (0-35%). *Brizalina subaenariensis* appears at 34 cm depth and becomes co-dominant (20 to 60%) in the upper part of core. *Bulimina exilis* also appears in the upper part of the core and rapidly becomes a significant component of the assemblage (up to 30%). The occurrence and increased relative abundance of *Brizalina subaenariensis* and *Bulimina exilis* in the upper part of the core are consistent with a high organic carbon flux and low dissolved oxygen concentrations (Kaiho, 1994; Bruchert et al., 2000).

4.1.4. Geochemistry

The organic carbon content of the sediment increases from 1.1-1.2% in the lower part of the core (i.e., below 30 cm) to 1.6% in the upper 5 cm (Figure 6) of core AH00-2220. This would correspond to an increase of the carbon mass accumulation rate (MAR) from < 0.01 to values between 0.02 and 0.035 g $cm^{-2}yr^{-1}$.

The $\delta^{13}C_{org}$ values fluctuate between -25.2 and -24.0‰ throughout the core. In the lower part of the core (i.e., from 20 to 50 cm), there is a gradual lowering of the isotopic signature from -24.2 to -25.2‰, whereas $\delta^{13}C_{org}$ values increase from -24.9 to -24‰ towards the top of the sequence. The C_{org}:N ratios are variable, ranging from 11 to 15, but they increase stepwise from the base to the top of the core. In the top 20 cm, the $\delta^{13}C_{org}$ values and C_{org}:N ratios appear to reflect opposite trends, the former shifting to more marine values whereas the latter drifts towards more continental values.

4.2. Core CR02-23

4.2.1 Chronology

The $\ln(^{210}Pb_{ex})$ is constant in the top 3 cm (Figure 7), which corresponds to the interval of active bioturbation. Throughout the 3-11 cm depth interval, $\ln(^{210}Pb_{ex})$ decreases smoothly and the linear regression yields a slope of -0.074 (r^2 = 0.92), corresponding to a sedimentation rate of 0.42 (± 0.04) cm/yr, similar to the rate estimated at AH00-2220. According to this age model, the upper 10 cm would represent about 24 years of sedimentation (i.e., 1978-2002 AD) whereas the upper 30 cm would correspond to nearly 72 years of sedimentation (i.e., 1930-2002 AD).

4.2.2 Palynology

There is a rapid increase of dinocyst concentrations toward the top of the core in the upper 10 cm (Figure 8) whereas concentrations are fairly uniform (1000-1400 cysts g^{-1}) in the 10-50 cm interval. The assemblages are dominated by the heterotrophic genus *Brigantedinium* (55 to 85%). It is accompanied by other heterotrophic taxa such as *Selenophemphix quanta, Islandinium minutum* and *Islandinium? cezare*. Some autotrophic taxa are present, notably *Nematosphaeropsis labyrinthus, Pentapharsodinium dalei, Operculodinium centrocarpum, Spiniferites elongatus* and *Spiniferites ramosus*. No major change in the assemblages can be distinguished, except an increase of some autotrophic taxa, *Pentapharsodinium dalei* (2 to 10%) and *Nematosphaeropsis labyrinthus* (1 to 7%), and a concomitant decrease of heterotrophic taxa *Brigantedinium* spp. (80 to 60%), *Selenophemphix quanta* (25 to 10%) and *Islandinium minutum* (10 to 3%) in the top 5 cm of the core.

4.2.3 Benthic foraminiferal assemblages

The concentration of benthic foraminifera tests ranges from 5 to 8 tests/g in the lower and middle part of the core, and increases up to 50 tests/g in the upper 10 cm (Figure 9). The concentrations of foraminifera organic linings recovered from the palynological preparation decrease significantly in the upper part of the core. *Globobulimina auriculata* dominates the tests assemblages from the base of the core to 10 cm, with relative abundances varying between 40 and 100%. *Brizalina subaenariensis* and *Bulimina exilis* appear at about 25 cm and become abundant (up to 40% and 28%, respectively) in the upper part of the core. The *Bulimina marginata* taxon is present throughout the core with variable abundances, between 0 and 40%.

4.2.4 Geochemistry

The organic carbon content of the sediment increases from 1.3% at the base of the core to 1.9% in the upper part of the core (Figure 10). The $\delta^{13}C_{org}$ ranges from -24.2 to -24.6‰ below 30 cm, decreases slightly towards the surface in the 10 to 30 cm interval and increases sharply from -24.6 to -23.5‰ in the top 10 cm. The C_{org}:N ratio profile is an amplified, mirror image of the $\delta^{13}C_{org}$ profile, it shows little variation (i.e. 12.5 ± 0.5) below 30 cm, increases from 13 to 15 towards the surface in the 10 to 30 cm interval, and decreases sharply thereafter (i.e., from 15 to 13) towards the sediment-water interface.

5. Discussion

5.1 Chronology of cores

Geochemical data (^{210}Pb) reported from three sites sampled between 1986 and 2000 in the LSLE show a clear oceanward decline of the sedimentation rate: from 0.54-0.71 cm/yr at station G2 (here core CR02-25 in Figure 1) to 0.29-0.45 cm/yr at station

23 (here core CR02-23) to 0.10-0.22 cm/yr at station 009 at the end of the LSLE in front of Pointe-des-Monts (Deschamps, 1997; Smith et al., 1999; Zhang, 2000; Silverberg et al., 1986; Jennane, 1992). The sedimentation rates obtained in the present study are consistent with these previous estimates: estimated sedimentation rates in the upper parts of core AH-2220 (located between core CR02-25 and CR02-23) and core CR02-23 are 0.50 cm/yr and 0.42 cm/yr, respectively.

5.2 Organic matter flux

Export of organic carbon production can be inferred using a variety of proxies, such as mass accumulation rates of organic carbon (Sarnthein et al., 1988; Pedersen, 1983) and micropaleontological tracers of benthic production (Loubere and Fariduddin, 1999). The organic carbon content increases gradually towards the sediment-water interface, from 1.1% to 1.6% in core AH00-2220 and from 1.3% to 1.9% in core CR02-23. In the former, this corresponds to an increase in MAR from 0.01 to ~0.02-0.035 g/cm^2*yr.

The increase of Corg content in the upper part of the cores may simply reflect the progressive remineralization of OC buried in the sediment and, thus, the use of diagenetically-independent tracers of organic matter flux is critical. In this study we used micropaleontological tracers of OC fluxes, more specifically, the abundance of benthic foraminifera, a component of the benthic population that relies on the supply of detrital, labile organic matter to the sea floor as a food source (Loubere and Fariduddin, 1999). We used both the abundance of calcareous and agglutinated shells as well as the concentration of foraminifera organic linings. Both tracers, especially the latter, are more resistant to diagenetic degradation (e.g., dissolution or oxidation) than the accumulated organic carbon (Corliss and Chen, 1988).

As demonstrated in several studies (Altenbach, 1988, 1992; Lee, 1974; Gooday, 1986, 1988, 1994), the concentration and AR of benthic foraminifera vary mainly as a direct function of organic matter supply to the sea floor. Under this premise, the up to

one order of magnitude increase in concentration and AR of benthic foraminifera tests and linings observed over the last three decades in the sediments of the LSLE can be interpreted as a response to an increased labile organic carbon flux. Alternatively, it could be interpreted as a better preservation and/or lesser predation of the foraminifera (Verhallen, 1991) but, given the ten-fold increase in concentration, it is not likely that they solely account for such a gradient. Furthermore, it is important to note that the gradient also corresponds to the occurrence, among the benthic assemblages, of two species that are tolerant of lower oxygen levels (see section 5.3).

5.3 Primary productivity

The carbon isotopic signature of the sedimentary organic matter is diagnostic of its origin and, thus, the integrated contribution of its various sources (Meyers, 1994). In estuarine environments, the carbon isotopic signature reflects the proportion of particulate and dissolved organic carbon (POC and DOC) derived from both terrestrial sources and *in-situ* (i.e., algal) production (Mook and Koene, 1975; Westerhausen et al., 1993). Marine algae are typically composed of OC with a ^{13}C isotopic composition of -20 to -22‰ whereas continental OC is lighter at -27‰ (Meyers, 1994). The shift in $\delta^{13}C_{org}$ recorded in the upper part of the core, over the 0 to 20 cm interval, may therefore be interpreted as a higher contribution of marine organic carbon to the sediments of the LSLE since the 1960s. The interval below is characterized by the opposite trend, which may reflect the rapid growth of the paper mill industry from the 1930's to the 1950's and a corresponding increase in the discharge of terrestrial organic matter to the estuary (St-Onge et al., 2003). These pre-1960 and post-1960 trends are also observed in the C_{org}:N ratio profile in core CR02-23, but not in core AH00-2220. The discrepancy may reflect the spatial heterogeneity in the water column chemical properties and circulation patterns in this part of the estuary (El-Sabh and Silverberg, 1990). The C_{org}:N ratio profile in core AH00-2220

in more consistent with other geochemical and micropaleontological proxies at is shows an increase from the bottom of the core to about 10 cm below the surface, thus alluding to more important continental inputs before ca. 1960 AD, and a relatively greater marine organic carbon source over the last decades.

Variations of the dinoflagellate cyst concentrations and ARs can also be qualitatively linked to primary production as dinoflagellates, together with diatoms and coccolithophores, are the main primary producers in marine environments (e.g., Parson et al., 1984). Along the Norwegian margins, recent increases in dinoflagellate cyst concentrations in the sediments were linked to regional eutrophication and stimulation of the algal population growth (Dale and Fjellså, 1994). The two to three-fold increases in dinocyst concentration and AR observed over the last three decades in core AH00-2220 and in the upper 20 cm of core CR02-23 most likely reflect an increase in dinoflagellate production and, thus, in primary productivity, possibly related to eutrophication. Sedimentation rate independent estimates of dinocyst production, based on relative variations of the dinocyst:pollen ratio in the sediments, further support this interpretation.

Dinoflagellates cysts are made of refractory organic matter (sporopollenin) and, thus, preservation is generally very good in sedimentary marine environments, especially in water with low oxygen content and high sedimentation rate. Given that we found an abundance of the ''fragile'' cysts *Brigantedinium* spp. and other *Protoperidium* species, among the more oxygen sensitive cysts (e.g. Zonneveld, 2000), we are confident of our assumption about good preservation. The same argument applies to the benthic foram organic linings whose preservation is not affected significantly during early diagenesis.

In addition to autotrophic taxa, the dinoflagellate population includes heterotrophic species that feed on diatoms (Dale, 1996; Sætre et al., 1997; Jacobson and Anderson,

1986). Their cysts, preserved in the sediments, are particularly abundant in polynyas (Hamel et al., 2002) and upwelling areas (Radi and de Vernal, 2004) and constitute indirect tracers of productivity. No obvious change in the relative abundance of heterotrophic versus autotrophic dinocysts was noted in the analysis of the cores retrieved from the LSLE. The small changes in the relative abundance of the dinocyst taxa over time may reflect changes in hydrographic conditions such as the warming of LSLE waters by ~1°C between 1960-2000 (NODC, 2001). The differences in dinocyst assemblages that are observed in the two cores further emphasize the spatial heterogeneity in surface water properties in the LSLE, as noted by Giroux (1990) on the basis of a clear zonation of dinocyst assemblages, notably for *Pentapharsodinium dalei* taxa.

5.4 Dissolved oxygen concentration

Many authors have reported relationships between the composition of benthic foraminiferal assemblages and bottom water dissolved oxygen concentrations (for a review see: van der Zwaan, 1999). The two cores analyzed in this study reveal an increase in benthic foraminifera abundances toward the surface and a clear taxonomic zonation: *Brizalina subaenariensis* and *Bulimina exilis* appear roughly at the same time (~1960 AD in core AH00-2220 and ~1955-1960 AD in core CR02-23) and their relative abundances increase towards the surface. The appearance of these species reflects significant changes in the bottom water conditions. They are both considered to be low-oxygen tolerant (Kaiho et al., 1994; Bruchert et al., 2000), an observation that is consistent with the progressive depletion of dissolved oxygen in the bottom waters of LSLE documented by Gilbert et al. (2005).

6. Conclusions

Micropaleontological and geochemical analyses of sediment cores collected in the Lower St. Lawrence Estuary provide consistent evidence for a significant change in environmental conditions over the last decades. These include:

(a) Recent increase of the organic matter flux to the sediment, as reflected by their organic carbon content and accumulation rate as well as by the abundance of benthic foraminifera whose proliferation is dependent upon the organic carbon supply to the sea floor.
(b) Increased marine biogenic productivity over the last 3 decades, as indicated by the isotopic signature of the preserved OC and the increased accumulation rate of dinoflagellate cysts.
(c) Depletion of dissolved oxygen in the bottom waters, as revealed by the occurrence of low-oxygen tolerant foraminifera *Brizalina subaenariensis* and *Bulimina exilis*.

These observations are consistent with the hypothesis that a recent eutrophication in the Lower St. Lawrence Estuary may, at least in part, be responsible for the progressive depletion of dissolved oxygen concentrations in the bottom waters. Nevertheless, the spatial extent of this eutrophication signal within the Estuary and Gulf of St. Lawrence and the origins of the increased primary productivity remain to be addressed.

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Figure 1. Map showing the Lower St. Lawrence Estuary and the location of the coring sites. The bathymetric contour represents 200 meters. Dots represent coring sites and stars represent largest nearby cities.

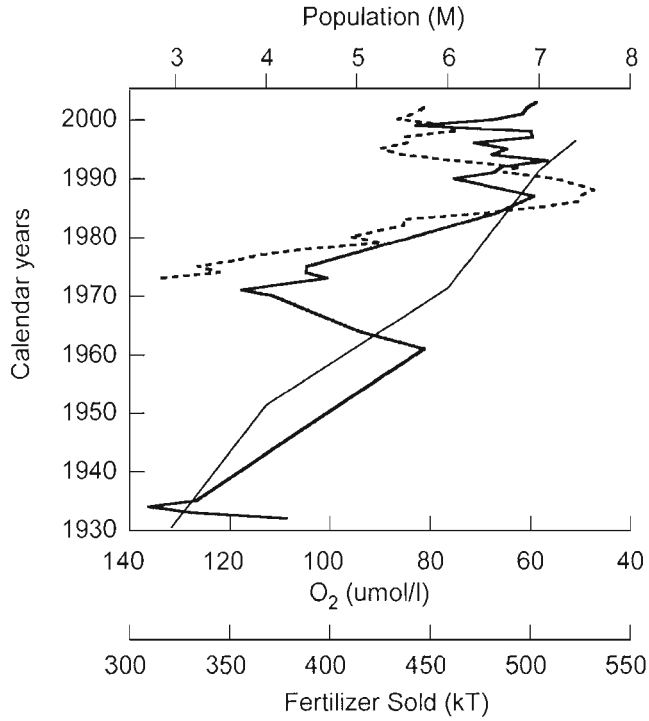

Figure 2. Quebec population growth (thin line), local fertilizer purchases (dotted line) and DO content of the LSLE bottom waters (bold line) since 1930 (Statistics Canada, Fertilizer Trade, Catalogue 46, 207; Quebec manufacturers association report, 2001; Gilbert et al., 2005).

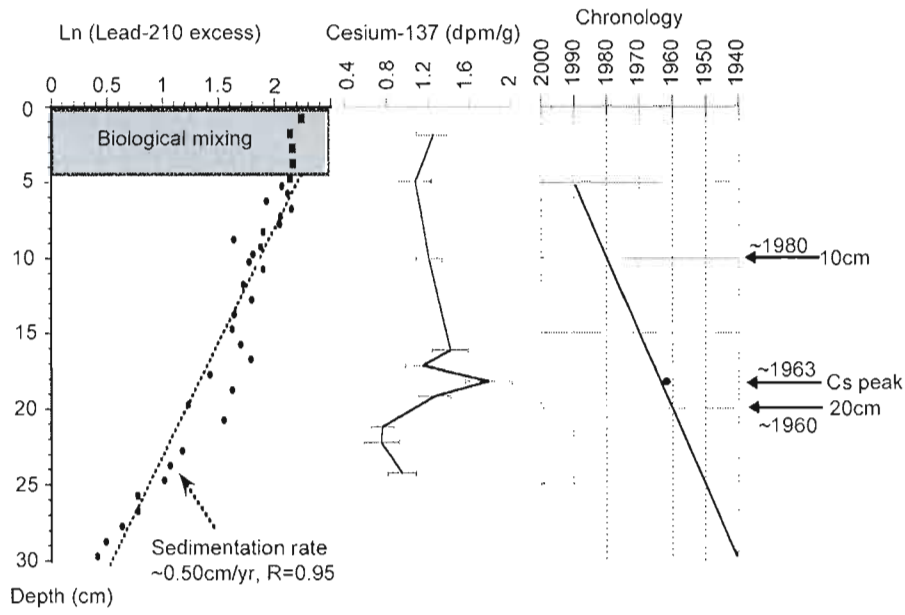

Figure 3. Excess lead-210 (ln) as a function of depth in core AH00-2220. Squares represent samples from the bioturbated zone, not taken into account in the sedimentation rate calculation. The dotted line is the linear regression used to derive the sedimentation rates. Cesium-137 activities as a function of depth in core AH00-2220 are also shown as well as the age model for box core AH-2220 as a function of depth based on lead-210 (line) and cesium-137 (dot).

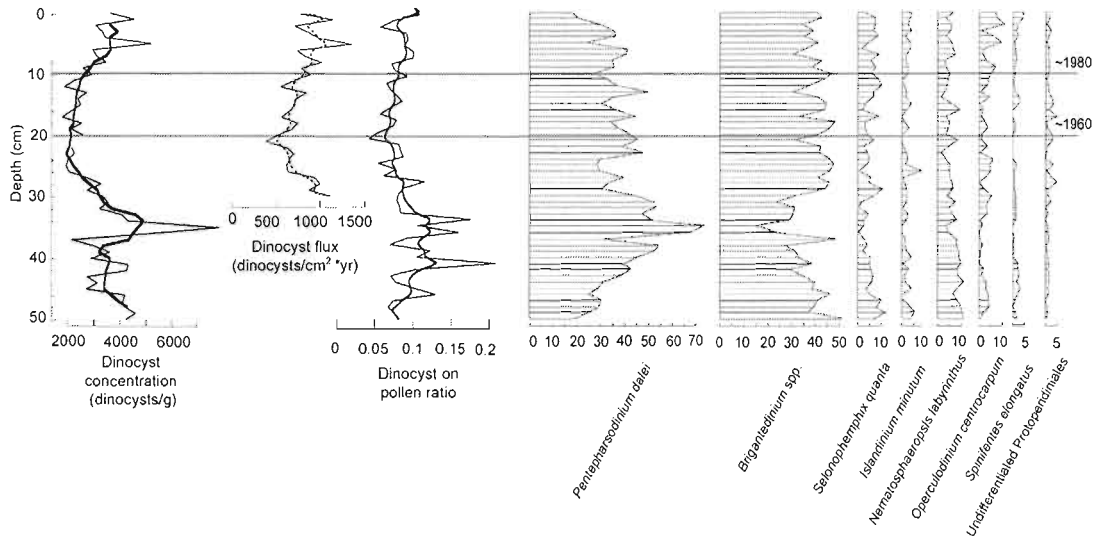

Figure 4. Dinoflagellate concentration (cysts/g), cyst AR (cysts/cm^2.yr), dinocyst:pollen ratio and percentages of most abundant taxa as a function of depth in core AH00-2220. The bold and dotted curves correspond to 5-point running means for concentration and AR, respectively.

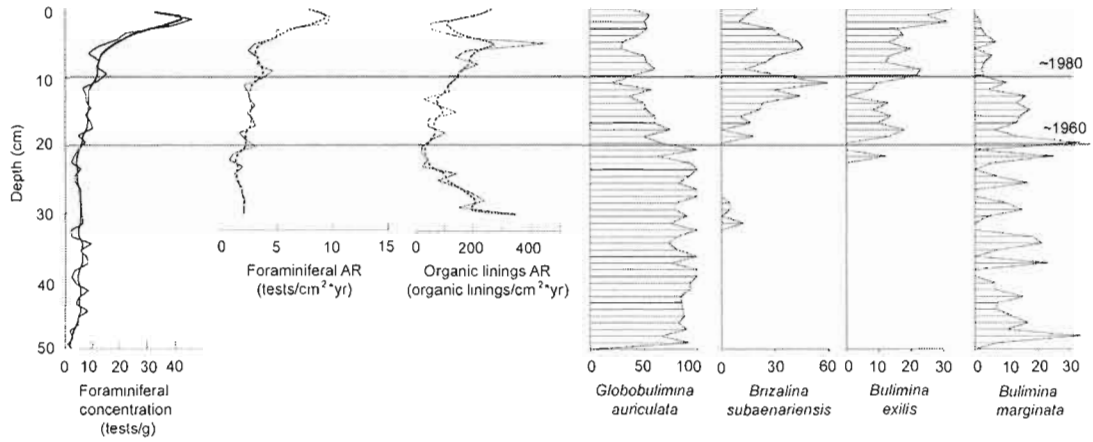

Figure 5. Benthic foraminifera concentration (tests/g), AR (tests/cm^2.yr), organic lining AR (OL/cm^2.yr) and percentages of most abundant taxa as a function of depth in core AH00-2220. The bold and dotted curves correspond to 5-point running means for concentration and AR, respectively.

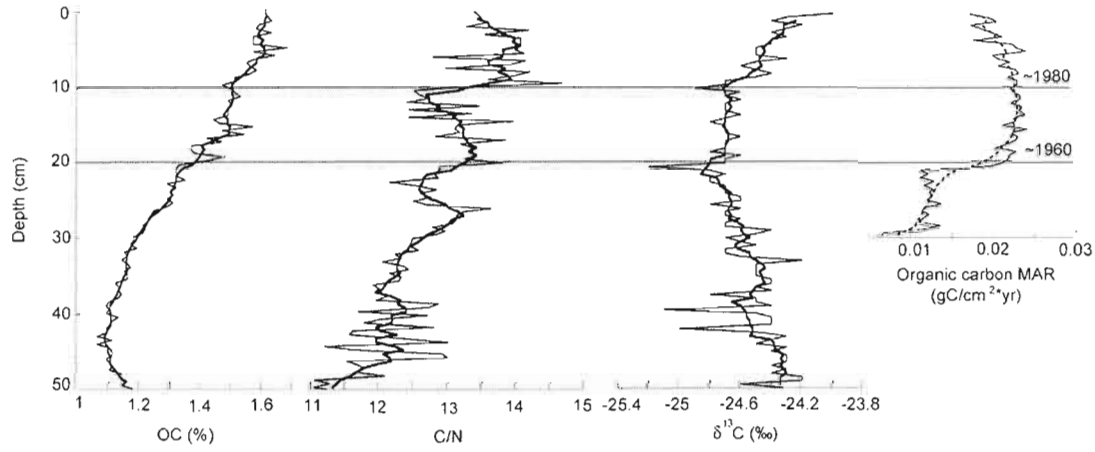

Figure 6. Organic carbon (OC) content, C_{org}/N ratio, $\delta^{13}C$ of organic carbon and MAR of organic carbon as a function of depth in core AH00-2220. The bold and dotted curves correspond to 5-point running means for concentration and MAR, respectively.

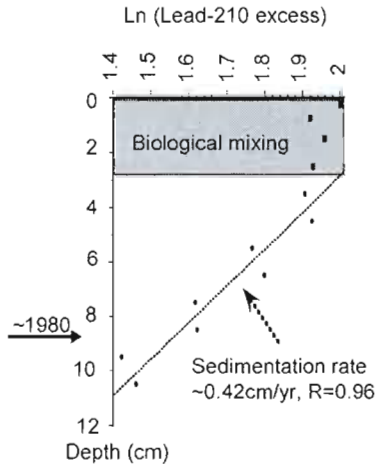

Figure 7. Excess lead-210 (ln) as a function of depth in core CR02-23. Squares represent samples from the bioturbated zone, not taken into account in the sedimentation rate calculation. The dotted line is the linear regression used to compute the sedimentation rate.

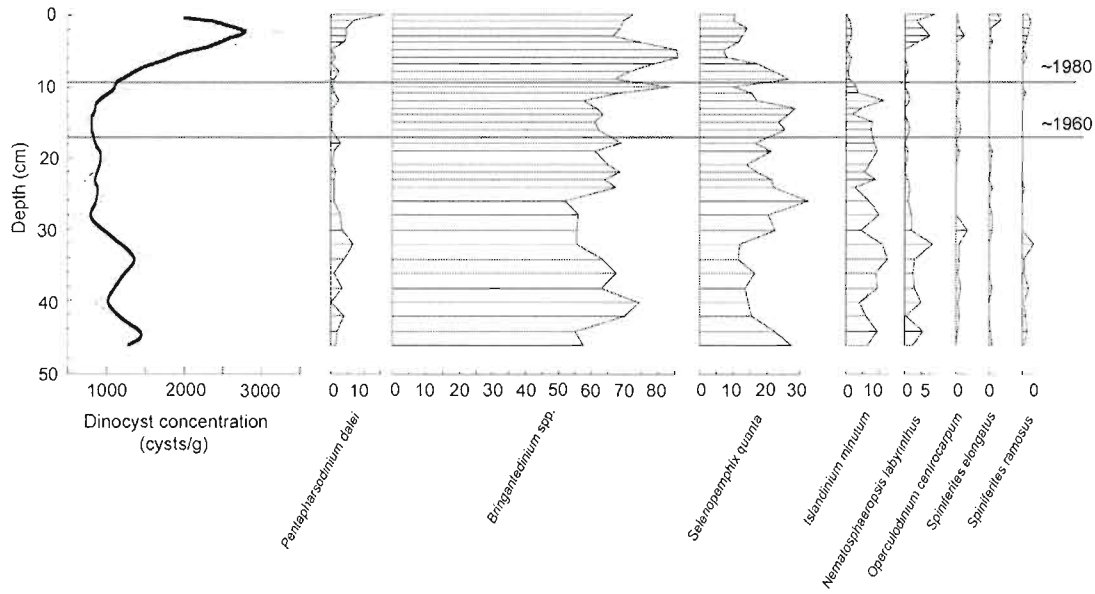

Figure 8. Dinoflagellate cyst concentration (cysts/g) and percentages of most abundant taxa as a function of depth in core CR02-23. The bold line represents a 5-point running mean.

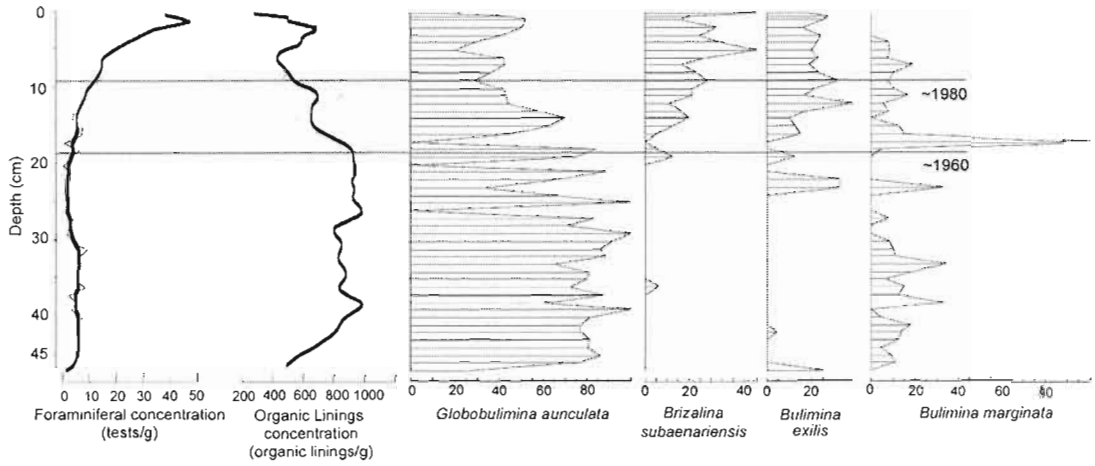

Figure 9. Benthic foraminifera concentration (tests/g), organic lining (OL) concentration (OL/g) and percentages of most abundant taxa as a function of depth in core CR02-23. Bold lines represent 5-point running means.

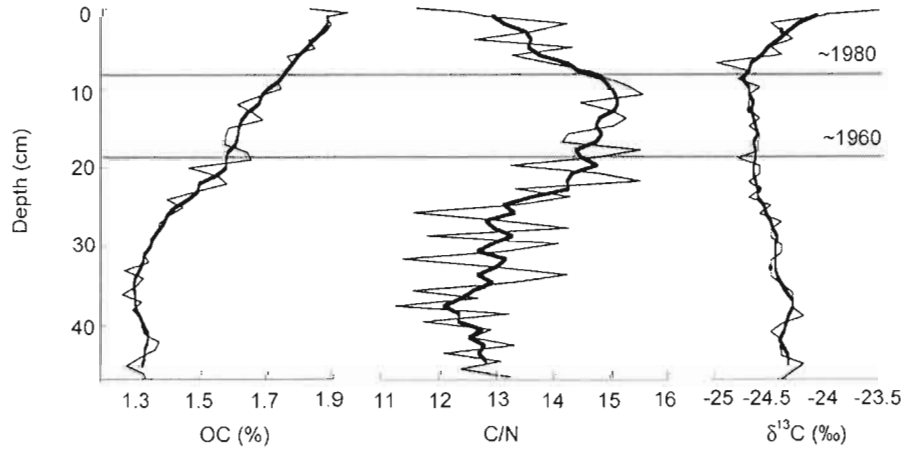

Figure 10. Organic carbon (OC) content, Corg/N ratio, and $\delta^{13}C$ of organic carbon as a function of depth in core CR02-23. Bold lines represent 5-point running means.

CONCLUSION

En résumé, notre étude sur des sédiments de l'EMSL met en évidence des changements environnementaux significatifs depuis les dernières décennies, en particulier :

(a) Une augmentation récente des accumulations de matière organique mesurée par la teneur en carbone organique ainsi que par les foraminifères benthiques qui dépendent des apports de matière organique.

(b) Une augmentation de la productivité primaire au cours des dernières décennies telle qu'indiqué par la signature isotopique de la matière organique et par l'augmentation du taux d'accumulation des kystes de dinoflagellés.

(c) Une diminution des concentrations en oxygène dissous à l'interface eau-sédiment telle qu'indiquée par l'apparition et la prolifération des espèces de foraminifères benthiques Brizalina subaneriensis et Bulimina exilis.

Cette étude tend donc à démontrer une tendance récente vers une eutrophisation dans l'estuaire du Saint-Laurent, résultant en une importante modification des conditions d'oxygénation à l'interface eau-sédiment. Il devient donc très important de suivre l'évolution de cette masse d'eau car le niveau d'oxygénation devient alarmant pour l'écosystème du Saint-Laurent. Une étude plus approfondie de l'origine et de l'étendue spatio-temporelle de l'hypoxie et de l'eutrophisation dans l'estuaire et le Golfe est nécessaire pour pouvoir préparé un plan de revalorisation de la zone touchée. Il serait aussi avisé d'étudier la dynamique des différents nutriments qui pourraient être la cause de l'eutrophisation, comme l'azote.